CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
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THE DECOMPOSITION OF MERCUROUS CHLORIDE BY DISSOLVED CHLORIDES: A CONTRIBUTION TO THE STUDY OF CONCENTRATED SOLUTIONS.

By Theodore William Richards and Ebenezer Henry Archibald.

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Introduction.

Long ago Miahle observed that a concentrated solution of common salt acts upon calomel with the formation of small amounts of mercuric chloride.[*]   Many years afterwards, one of us,[†] without knowing of his work, rediscovered this reaction, and found that the fluctuations in the potential of the "normal calomel electrode" of Ostwald, are due to its disturbing influence.   At that time it was shown that the reaction is much diminished by dilution, and hence that a decinormal solution is far better as an electrolyte than a normal solution.   The "decinormal electrode," thus recommended for the first time, has since come into common use.

It was shown also that neither light nor oxygen are important causes in effecting the decomposition, but that the reaction is much furthered by increase of temperature.   No attempt was made at the time to fathom the matter, but a suggestion was made that the reaction might be due to the catalytic action of the ionized chlorine of the dissolved chloride.

The investigation of the problem which was at that time promised has now been continued, and the object of this paper is to show that while the second condition of this suggestion seems probable, the first does not hold. Another example is thus afforded of the frequently recurring circumstance of the removal of a reaction from its classification among catalytic phenomena after better acquaintance with its nature.

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[*] Miahle, J. Pharm., **26**, 108; Ann. Chim. et Phys. (3), **5**, 177 (1842).
[†] Richards, These Proc., **33**, 1 (1897); Z. phys. Ch., **24**, 39.

The method employed was to treat calomel with solutions of chlorides of various concentrations for varying times, and to determine the extent of the reaction by determining the amount of mercury dissolved.

PREPARATION OF MATERIALS.

Mercury already very pure was thoroughly freed from the possible presence of substances with greater solution-tension by treatment with sulphuric acid and potassic dichromate, and subsequent spraying through ten per cent nitric acid. Calomel was resublimed at as low a temperature as possible, and thoroughly washed with water and with the solution to be used in each particular case. One of us had previously shown that the source of the calomel is immaterial.* Sodic chloride was precipitated by pure hydrochloric acid from a saturated solution of the so-called "chemically pure" salt. It was then twice recrystallized from water, and thoroughly dried to drive off any possible traces of acid. Pure calcic nitrate was made by many recrystallizations; this was converted into carbonate, and the carbonate converted again into chloride. Several recrystallizations freed this chloride from every trace of the nitrate or of ionized hydrogen. Baric chloride was crystallized first from a solution strongly acid with hydrochloric acid, and subsequently from aqueous solutions by precipitation with pure alcohol. It also was wholly neutral to methyl orange. Cadmic chloride was made by dissolving the pure metal in pure acid and recrystallizing twice. The salt was dried thoroughly in order to make certain of the absence of ionized hydrogen, which is less easily detected in this case. Hydrochloric acid itself was purified by redistillation, the purest acid of commerce serving as the starting-point.

APPARATUS AND METHOD OF ANALYSIS.

It was necessary to digest the mixtures for long periods of time at a constant temperature. For this purpose they were placed in large test-tubes of sixty cubic centimeters capacity arranged to rotate transit-fashion in an Ostwald thermostat after the manner suggested by Schröder.† In the case of the weaker solutions several of these tubefuls were used for each analysis, but with the stronger solutions fifty cubic centimeters sufficed. The tubes were corked with rubber stoppers

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* Richards, loc. cit.

† Richards and Faber, Am. Ch. J., 21, 168 (1899). The thermometer used to register the temperature was of course suitably verified.

which had previously been boiled with dilute alkali and scrupulously rubbed and washed. Into each tube was placed a large excess of calomel, about a decigram of mercury, and fifty cubic centimeters of one of the solutions of chlorides.

After a slight shaking, the settled precipitate was always covered upon standing with a layer of gray partially reduced material, which settled more slowly and hence gave more opportunity for reduction. When the equilibrium was completed by prolonged shaking, this gray material was mixed evenly throughout, and no longer appeared on the surface of the precipitate. Thus the absence of a gray film on settling was a rough guide to the completion of the reaction.

After five or six hours of agitation in the thermostat at $25.^\circ \pm 0.05^\circ$ one of the tubes was opened, its contents filtered, and the dissolved mercury determined analytically. At intervals of an hour successive tubes were similarly treated, and after seven or eight hours no change was found in any case. Evidently a state of equilibrium is soon attained, and the reaction cannot be called catalytic. The values given below are of course the values corresponding to this maximum.

In this paper no evidence is given concerning the size of the grains of calomel. Ostwald [*] has recently shown that this may be an important factor in determining the concentration of a saturated solution, and hence in fixing the basis of the present equilibrium. Concerning this point it need only be said that while the *absolute* extent of solubility may vary with the size of the grains, the *relative results*, upon which alone the conclusions of this paper are founded, are not affected. This is the case because the same preparation of calomel was used in every instance. Moreover, since the calomel was sublimed and since it is notoriously difficult to powder, the individual diameters could not have been very small, hence a value approximating that corresponding to a flat surface must have been obtained.

A number of experiments indicated that the mercury salt thus dissolved was in the mercuric rather than in the mercurous state. The visible deposition of mercury during the reaction is alone almost enough to prove this. Moreover, neither permanganate nor bichromate suffered more than the faintest trace of reduction upon addition to a solution which contained much dissolved mercury. The minute trace of decolorization which was observed was no greater than that produced by a solution of mercurous chloride in pure water. On the other hand, small

[*] Zeitschr. phys. Chem., **34**, 495 (1900).

amounts of stannous chloride gave plentiful white precipitates of calomel.

In all cases except that of cadmium, the mercuric salt in solution was determined as sulphide. The black precipitate produced by hydrogen sulphide was collected on a Gooch crucible, washed with alcohol, carbon disulphide, and again with alcohol, and finally dried at 100°. Satisfactory agreement between parallel analyses, which were almost always made in duplicate, was obtained. In the tenth-normal solutions of sodic chloride the amount of mercuric chloride was too small to be collected, hence it was determined colorimetrically by comparison with known solutions of similar dilution.

The following table explains itself. The last-column contains an arbitrary ratio which is an index of the changing relationship between the amounts of mercuric chloride formed and the amounts of sodic chloride present. The values in the third column were calculated from those in the second; and the values in the fifth column from those in the third and fourth.

MERCURIC CHLORIDE FOUND IN SOLUTIONS OF SODIC CHLORIDE.

No. of Exp.		Wt. of Solution taken.	Vol. of Solution.	Wt. of HgS found.	Wt. of $HgCl_2$ in 1 Litre of Solution.	c Mean Wt. of $HgCl_2$ in 1 Litre.	C Conc. of NaCl Solution in Equiv. Grams.	$1000\,\dfrac{c}{C}$ Milligrams $HgCl_2$ for every Mol. NaCl.
		grm.	c. c.	m. g.	grm.	grm.	equiv.	
1		...	...	...	0.0041	0.0041	0.10	41.0(?)
2	a	64.5	62.0	2.2	0.041	0.041	1.00	41.5
	b	66.1	63.5	2.3	0.042			
3	a	65.9	61.1	6.8	0.130	0.129	2.00	64.5
	b	80.3	74.5	8.2	0.128			
4	a	75.4	68.8	11.4	0.194	0.194	2.50	77.6
	b	83.0	75.7	12.6	0.194			
5	a	73.8	64.6	21.1	0.382	0.380	3.80	100.0
	b	80.3	70.3	22.8	0.379			
6	a	58.7	49.4	27.2	0.642	0.643	5.00	128.6
	b	69.7	58.8	32.5	0.644			

These facts, together with similar facts concerning solutions of three other chlorides, are represented in the accompanying diagram.   Evidently the first parts of the four curves are very similar in tendency, but as the highest concentrations are reached, the curves develop individuality.

MERCURIC CHLORIDE FOUND IN VARIOUS SOLUTIONS.
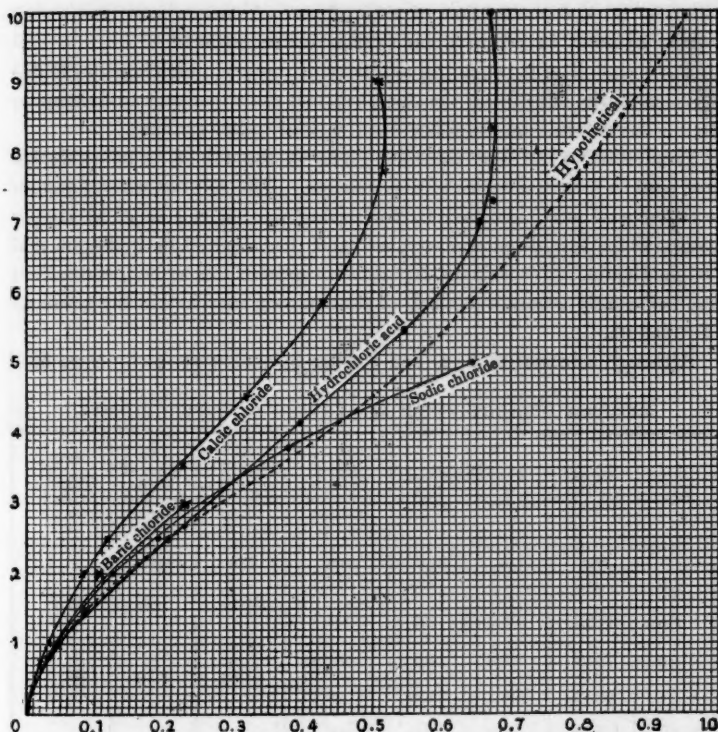
The ordinates represent equivalent concentrations of the solvent chlorides, and the abscissae represent grams of mercuric chloride per litre of solution.   The data for baric, calcic, and hydric chlorides are to be found on pages 352, 353, and 354.

Manifestly some particular property of the several solutions must be responsible for the reaction; and since the reaction results in raising the quantivalence of the mercury, it may be concluded that the particular property in question is the tendency of some molecular species already in the solution to combine with mercuric chloride.

This conclusion concerning the action of the substances on *mercurous* chloride is reinforced by the facts concerning the extent to which *mercuric* chloride is dissolved by solutions of various chlorides. Solutions of sodic chloride dissolve amounts of mercuric chloride which increase with the amounts of common salt present, until the saturation point is reached, while solutions of hydrochloric acid dissolve a maximum of mercuric chloride at a concentration of acid of seven times normal, remaining almost constant in action upon further concentration.[*]

The parallelism between the tendency of these soluble chlorides to dissolve mercuric chloride on the one hand, and their tendency to decompose mercurous chloride on the other hand, is thus rather striking.

In addition to the four chlorides given in the tables, cadmic chloride was used in a special series of experiments. The solution after digestion with calomel was analyzed by immersing in it a roll of clean copper gauze, which was dried and weighed, and then ignited in hydrogen and weighed again. Preliminary experiments showed this to be a convenient and sufficiently accurate method of determining mercury in the presence of cadmium.

Although solutions of 2, 4, and 8 times normal were used, in no case

MERCURIC CHLORIDE FOUND IN SOLUTIONS OF BARIC CHLORIDE.

No. of Exp.		Wt. of Solution taken.	Vol. of Solution.	Wt. of HgS found.	Wt. of $HgCl_2$ in 1 Litre of Solution.	c Mean Wt. of two Det. of $HgCl_2$ in 1 Litre Solution.	C Conc. of $BaCl_2$ Solutions in Equiv. Grams.	$1000 \frac{c}{C}$ Milligrams $HgCl_2$ for every ½ Mol. $BaCl_2$.
		grm.	c. c.	m. g.	grm.	grm.	equiv.	
1	a	106.5	97.8	3.6	0.043	0.044	1.00	44.0
	b	112.0	103.0	3.9	0.045			
2	a	101.8	89.8	6.7	0.087	0.088	1.50	58.6(?)
	b	120.3	106.1	8.0	0.088			
3	a	94.5	80.2	7.3	0.106	0.107	2.00	53.5
	b	112.8	95.7	8.8	0.107			
4	a	131.2	103.8	20.5	0.231	0.231	3.00	77.0
	b	106.8	84.5	16.7	0.231			

[*] Homeyer and Ritsert, Pharm. Ztg., **33**, 738, quoted by Comey, Dict. of Solubilities, 227 (1896).

Ditte, Ann. Chim. phys., (5) **22**, 551; Engel., ibid. (6), **17**, 362. See Comey, as above.

could a trace of mercury be detected in the solution.   Moreover, no gray precipitate of reduced mercury was ever observed when the cadmium solution was shaken with calomel in the first place.   One infers that there is not in dissolved cadmic chloride any considerable concentration of a molecular species capable of combining with mercuric chloride.

This conclusion is quite in accordance with the fact that the temperature-coefficient of the potential of the calomel electrode with solutions of cadmic chloride exhibits none of the irregularities observed when other chlorides are used.*

MERCURIC CHLORIDE FOUND IN SOLUTIONS OF CALCIC CHLORIDE.

No of Exp.	Wt. of Solution taken.	Vol. of Solution.	Wt. of HgS found.	Wt. of $HgCl_2$ in 1 Litre of Solution.	c Mean Wt. from two Det. of $HgCl_2$ in 1 Litre Solution.	C Conc. of $CaCl_2$ Solution in Equiv. Grms. ($\frac{1}{2} CaCl_2$).	$1000 \frac{c}{C}$ Milligrams $HgCl_2$ for every $\frac{1}{2}$ Mol. $CaCl_2$.
	grm.	c. c.	m. g.	grm.	grm.	equiv.	
1	. . .	. . .	. . .	0.022	0.022	0.72	31.6
2	. . .	. . .	. . .	0.033	0.033	1.00	33.0
3 $\{$ a	80.2	75.4	5.2	0.082 $\}$	0.081	2.00	40.5
b	75.6	69.3	4.7	0.079 $\}$			
4 $\{$ a	75.4	68.2	6.9	0.118 $\}$	0.118	2.50	47.2
b	78.4	70.9	7.2	0.118 $\}$			
5 $\{$ a	59.4	51.6	10.3	0.232 $\}$	0.231	3.52	65.6
b	61.5	53.5	10.8	0.230 $\}$			
6 $\{$ a	92.2	76.5	21.0	0.320 $\}$	0.322	4.64	69.3
b	99.4	82.5	22.8	0.323 $\}$			
7 $\{$ a	57.4	46.2	17.0	0.429 $\}$	0.430	5.85	73.4
b	67.0	53.9	19.9	0.431 $\}$			
8 $\{$ a	48.7	37.0	16.4	0.518 $\}$	0.518	7.80	66.4
b	76.4	58.1	25.8	0.519 $\}$			
9 $\{$ a	50.0	36.8	16.1	0.511 $\}$	0.510	9.00	56.6
b	47.5	34.9	15.2	0.509 $\}$			

* Richards, These Proceedings, **33**, 1 (1897).

INTERPRETATION OF RESULTS.

There are two possible interpretations of the phenomena under discussion. According to one, the undissociated mercuric chloride may be supposed to combine with the undissociated part of the electrolyte, forming an undissociated double salt, while according to the other, the undissociated mercuric chloride may be supposed to combine with the chlorine ion to form a complex ion. The following considerations attempt to decide which of these is more probable.

MERCURIC CHLORIDE FOUND IN SOLUTIONS OF HYDROCHLORIC ACID.

No. of Exp.		Wt. of Solution taken.	Vol. of Solution.	Wt. of HgS found.	Wt. of $HgCl_2$ in 1 Litre of Solution.	c Mean Wt. of $HgCl_2$ in 1 Litre of Solution.	C Conc. of HCl Solution in Equiv. Grams.	$1000 \frac{c}{C}$ Milligrams $HgCl_2$ for every Mol. HCl.
		grm.	c. c.	m. g.	grm.	grm.	equiv.	
1		...	...	...	{ 0.034 0.034 }	0.034	0.83	41.0
2		...	...	...	{ 0.048 0.048 }	0.048	1.00	48.0
3	a	132.0	126.7	22.4	0.206	0.207	2.50	83.0
	b	179.0	171.8	30.6	0.208			
4	a	74.5	69.7	23.9	0.400	0.399	4.15	96.1
	b	87.8	82.0	28.0	0.398			
5	a	85.2	78.1	36.6	0.548	0.548	5.48	100.0
	b	75.8	69.5	32.6	0.548			
6	a	85.4	76.8	42.9	0.653	0.654	7.00	92.8
	b	90.4	81.3	45.5	0.655			
7	a	82.6	73.8	42.7	0.676	0.675	7.30	92.3
	b	95.6	85.5	49.3	0.673			
8	a	70.0	61.8	35.4	0.669	0.670	8.31	80.6
	b	95.8	84.6	48.6	0.671			
9	a	115.0	99.6	57.7	0.672	0.673	10.00	67.3
	b	123.0	106.5	61.4	0.674			

The shape of the first section of the curves, where the concentration of the mercury present increases at a greater rate than does the corresponding amount of electrolyte, suggests at first that the undissociated part of the latter is the portion concerned in the reaction ; but the curve representing a power of the concentration of the ionized chlorine has of course a similar tendency.

Hence the general shape of the curve is an insufficient basis for decision between the two hypotheses.

The fact that strong solutions of cadmic chloride have little or no influence on mercurous chloride supports the latter of the two hypotheses, since concentrated cadmic chloride solutions contain but a very small concentration of ionized chlorine.

More direct light upon the question is obtained by the measurement of electrolytic conductivity. According to the first hypothesis, which demands the presence of an undissociated double salt, the conductivity of salt solution should be considerably decreased by the addition of mercuric chloride. As a matter of fact, we found that the dissolving of mercuric chloride to saturation in a twice normal solution of common salt diminished but slightly the conductivity of the solution. The work of Le Blanc and Noyes * furnishes similar results concerning hydrochloric acid; and moreover these investigators showed by the catalysis of methyl acetate that the concentration of the hydrogen ion was undiminished by the addition of mercuric chloride. Hence the new compound is to be considered as highly ionized.

Yet further evidence is to be obtained by referring to the specific conductivities of strong solutions of the chlorides studied.† Here we find that while the conductivities of solutions of sodic and baric chlorides increase with the concentration as far as they may be followed, those of calcic and hydric chlorides exhibit maxima at a concentration about six times normal. The agreement between these maxima and those exhibited by our own curves at seven times normal is close enough to suggest an essential relation between the cause of conductivity and the cause of Miahle's reaction.
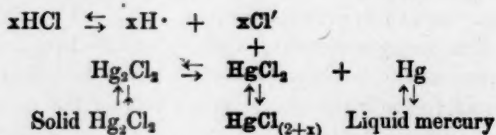
The evidence thus furnished is all consistent in indicating that the nature of the reaction is the addition of $HgCl_2$ to the chlorine ion, with the formation of a complex ion. This conclusion agrees with that of Le Blanc and Noyes, based upon other data.

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* Le Blanc and Noyes, Zeitschr. phys. Chem., 6, 389, seq. (1890).
† See Kohlrausch and Holborn (1898), Leitvermögen d. Electrol., pp. 145–154.

It remains now to detect the mechanism of the reaction. The work of Le Blanc and Noyes led them to believe that in dilute solutions containing an excess of the soluble electrolyte the new ion is bivalent, being formed by the reaction $2Cl' + HgCl_2 = HgCl_4''$. It will be shown that our own evidence supports this conclusion also.

The reaction with which we are concerned may perhaps be written thus: —

$$xHCl \leftrightarrows xH\cdot + xCl'$$
$$+$$
$$Hg_2Cl_2 \leftrightarrows HgCl_2 + Hg$$
$$\uparrow\downarrow \qquad\qquad \uparrow\downarrow \qquad \uparrow\downarrow$$
$$\text{Solid } Hg_2Cl_2 \qquad HgCl_{(2+x)} \quad \text{Liquid mercury}$$

The ion $HgCl_{(2+x)}$ will of course be the bearer of x negative charges of electricity. The above expression does not attempt completeness, but strives merely to represent the most essential features of the reaction in the simplest possible form.

The first conclusion to be noted is that the concentration of the uncombined but dissolved mercuric chloride will be constant, since it is formed by a reaction involving two precipitates. Hence the concentration of the ion $HgCl_{(2+x)}$ should vary as the concentration of the chlorine ion raised to the xth power.

It is immediately clear that x must be more than unity, for in the less concentrated solutions the concentration of the mercury present increases faster than that of the dissolving chloride, while the concentration of the ionized chlorine is supposed to increase less rapidly than the latter.

By taking $x = 2$ we obtain much more satisfactory agreement. If we assume that the concentration of the ions present is proportional to the specific conductivity,* we find that for solutions as far as twice normal the calculated curve agrees almost precisely with the actual amounts of mercury found. The specific conductivity of a twice normal solution of hydrochloric acid is 0.505, while that of a normal solution is 0.295. The squares of these numbers are respectively 0.255 and 0.087, two values which are very nearly proportional to the weights 148 and 48 milligrams of mercury per litre which were actually found to be dissolved from calomel by twice normal and by normal solutions of hydrochloric acid respectively.

With more concentrated solutions the results of this calculation agree

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* The possible dangers of this assumption are well known. It is made here simply in default of more certain knowledge.

less and less satisfactorily with the facts, the amount of mercury actually found always exceeding the calculated amount.   Evidently this disagreement may be due to the fact that some of the new complex acid remains in the undissociated state; the calculation considers only the ion, while the mercury weighed in analysis constituted the sum total.   The exact calculation of the amount undissociated is impossible for two reasons; in the first place, the mode of dissociation of such a tri-ionic compound as H_2HgCl_4 is uncertain; and in the next place, we have no data for the extent of the dissociation of the compound beyond the strength of a normal solution.

In spite of this double uncertainty, it is possible to make an approximate calculation.   This is sufficient to show that in a general way the argument is sound.   The approximate calculation is based upon the fact that so far as the extent of dissociation of the complex acid is known, it is equal to that of hydrochloric acid at the same concentration.[*]   On making the assumption that this relation holds in very strong as well as in moderately strong solutions, and waiving entirely the uncertainty as to the possible existence of the half-way ion $HHgCl_4'$, the proportion of the

APPROXIMATE CALCULATION OF THE TOTAL AMOUNT OF MERCURY.

Concentration of Hydrochloric Acid Solution or Gram-Equiv. per Litre.	κ = specific Conductivity of Hydrochloric Acid x.[†]	κ^2.	$a = \dfrac{\Lambda_v}{\Lambda_\infty}$.	$\dfrac{385\,\kappa^2}{a}$.	Milligrams Mercury found in 1 Litre Solution.[‡]
1	0.295	0.087	0.796	42	48
2	0.505	0.255	0.672	148	148
3	0.645	0.417	0.568	282	263
4	0.727	0.530	0.48	427	383
5	0.760	0.580	0.40	560	495
6	0.762	0.582	—	—	—
7	0.745	0.554	0.28	765	654
10	0.635	0.420	0.17	955	672

[*] Le Blanc and Noyes, loc. cit.

[†] These figures were obtained by graphic interpolation from the figures of Kohlrausch and Holborn, Leitvermögen d. Electrol., p. 154 (1898).

[‡] By interpolation.

undissociated complex may be calculated by simply multiplying the supposed concentration C of the ionized part of the complex by $\dfrac{1-a}{a}$, when a is the degree of dissociation of the acid. The total concentration of the mercury present would then be $C + C\,\dfrac{1-a}{a} = \dfrac{C}{a}.$ But if the new ion has the formula $HgCl_4''$, its concentration should be proportional to the square of the specific conductivity, κ, according to our previous reasoning. That is to say, $\dfrac{C}{a} = k\,\dfrac{\kappa^2}{a}.$* This equation is tested in the following table, by taking a value for the constant k which best satisfies the early part of the curve — namely 385.

The bearing of these rather discrepant figures is best seen by plotting the results. The curve which depicts the relation of the quantity $\dfrac{385\,\kappa^2}{a}$ to the concentration of the hydrochloric acid is indicated by a dotted line in the diagram on page 351. While with great concentrations it deviates considerably from the curve representing the amount of mercuric chloride formed by hydrochloric acid, it is nevertheless of the same general character. Considering the many uncertainties, including the doubt concerning the equation $a = \dfrac{\Lambda_v}{\Lambda_\infty}$, which interfere with its exact determination, the agreement is indeed as close as one has a right to expect.

Corresponding curves, with about the same degree of agreement, may be calculated for the other chlorides. It is perhaps worth while to call attention to the fact that the amount of mercury found in the most dilute solution studied, the tenth normal solution of sodic chloride, although very small, is too great to correspond to the theoretical value. The excess of about three milligrams per litre above the requirement of theory may well be due to dissolved calomel, which possesses a slight but unknown solubility of its own.†

All these arguments, reinforcing the conclusions which Le Blanc and Noyes reached from a different series of facts, seem to indicate that as

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* $k\,\dfrac{\kappa^2}{a} = k'\,\dfrac{\kappa}{V}$ because $a = \dfrac{\kappa V}{\Lambda_\infty}$ and $k' = k\,\Lambda_\infty$. The more complex form is retained because its meaning is the more obvious.

† The work of Kohlrausch and Rose (Zeitschr. phys. Chem. **12**, 241) is not conclusive concerning this solubility, since the behavior of calomel on solution is too little known. Their results seemed to indicate that the solubility amounted to three or four milligrams per litre.

nearly as the present means can determine, the reaction which we have been studying is to be thus represented in its simplest form : —

$$Hg_2Cl_2 + 2Cl' = Hg + HgCl_4''.$$
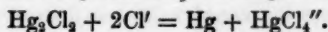
It is of interest to classify the equilibrium under consideration according to the Phase Rule of Willard Gibbs. Looked at from this point of view, we may speak of the system as consisting of four components, — water, soluble salt, mercury, and mercuric chloride. It is clear, therefore, that when we have together the four phases, — mercury, mercurous chloride, solution, and vapor, — at a fixed temperature, a single condition of freedom remains to be fixed in order to fix the system. The concentration of the ionized chlorine seems to supply this sixth ($n + 2d$) condition, determining the fixed points in the tables.

At the seven times normal point the concentration of the mercury dissolved seems to attain almost a constancy, being no longer increased by further addition of soluble electrolyte. According to the Phase Rule, such a phenomenon might be caused by the appearance of a new phase. This new phase would of course be one which would remove hydrochloric acid from the solution ; hence its presence or absence is easily discovered.

As a matter of fact, we found that after continued shaking with calomel, hydrochloric acid having an original concentration of 9.22 normal was reduced only to 9.20 normal. This is quite too small a difference to be due to the formation of a new phase; it must be ascribed either to adsorption by the calomel or to analytical error.

Hence the constancy of mercury dissolved is to be ascribed to conditions within the solution, and not to the appearance of a new phase.

Since the reaction seems to be effected primarily by the action of the chloride ion, it might be used to determine the concentration of the chloride ion, — or in the corresponding cases, that of the bromide or iodide ion. Especially would the case be applicable to the ionized chlorine because here the amount of mercury dissolved is too small to affect seriously other equilibria existing in the solution. Of course, with very dilute solutions the solubility of mercurous chloride itself would have to be taken into account.

This tendency of mercuric chloride to add to the chloride ion is a highly interesting circumstance. Other similar phenomena are being more and more frequently reported.* The tendency of cadmium to form

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* Cushman, Zeitschr. für anal. Chem., **34**, 368 (1895).

a similar complex ion is well known ; it has even been used by Cushman under Sanger's direction as a means of separating cadmium from other metals.   In this case the complex ion was formed simply by adding an excess of sodic chloride, which prevents cadmium from being precipitated by hydrogen sulphide.   Upon dilution the sulphide of cadmium begins to be precipitated, owing to the splitting apart of the ion in dilute solutions according to the law of "mass" action.

The same tendency has been used to explain the otherwise incomprehensible migration values of cadmium salts.   Very recently Noyes has shown that probably a similar ion, $BaCl_4''$,[*] exists in baric chloride solutions; and the migration values of concentrated calcic and magnesic chloride solutions lead one to infer that in these cases yet a greater concentration of $CaCl_4''$ and $MgCl_4''$ may exist.

It is interesting to note that the decomposition of the mercurous halide is carried to a much greater extent under similar conditions in the case of the bromide than in that of the chloride,[†] and yet further in the case of the iodide.   This may be due simply to the greater solubilities of mercurous bromide and iodide, but besides this cause there may exist a greater affinity of the molecule for the ion.   The study of the migration values of cadmium salts seems to show that the iodide has a much greater tendency to add to ionized iodine than the chloride has to add to ionized chlorine; and it is probable that the same relation exists in the case of mercury.

The facts recorded above show that an accurate quantitative analysis of a mercurous salt by precipitation with a soluble chloride is not to be expected, unless the chloride is added only in very slight excess, and then the solubility of mercurous chloride itself must be considered. When, however, a large excess of mercuric salt is present, as for example in the recent work of Ogg,[‡] it is obvious that the disturbing effect of the side-reaction must be much hindered, according to the law of "mass" action.

It is possible that the medicinal action of calomel is due to the small but definite concentration of mercuric complex salt produced by common salt or hydrochloric acid in the alimentary canal.   In any case, one is disposed to recommend cautious medicinal use of other chlorides in connection with calomel.

Preliminary experiments with sulphates showed that with these salts

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* A. A. Noyes, J. Am. Chem. Soc., 23, 37–57 (1901).
† Richards, loc. cit.
‡ Ogg, Zeitschr. phys. Chem., 27, 294 (1898).

the tendency to form complex compounds is much less than that exhibited by chlorides; hence the Latimer-Clarke and Weston cells are not much affected by this type of side-reaction.

The results of the present paper may be stated briefly as follows: —

1. The action of dissolved chlorides upon calomel is not catalytic, but results in the establishment of a definite equilibrium.

2. With equivalent solutions, less concentrated than five times normal, hydrochloric acid and sodic chloride have about equal tendencies to effect the reaction; baric chloride has less tendency, calcic chloride still less, and cadmic chloride no appreciable tendency.

3. The extent of the reaction in solutions not too concentrated is approximately a simple function of the square of the concentration of the chloride ion. This relation, taken in connection with a number of other considerations, points to the existence of a highly ionized complex $HgCl_4''$ in the solution, and thus confirms the work of Le Blanc and Noyes.

4. If approximate allowance is made for the probable concentration of undissociated complex salt present, all the figures, even as far as ten times normal solutions, seem to be explicable.

5. The suggestion is made that the reaction may be of use as a means of determining the concentration of the chlorine ion.

6. The corresponding reactions are much less marked with sulphates, but much more so with bromides and iodides.

7. Caution is needed when using mercurous chloride as a means of determining mercury in quantitative analysis.

CAMBRIDGE, 1899–1901.